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(54) **Coated article.**

(57) An article for use in high temperature corrosive environments is protected by successive coatings. The coatings comprise

i) a first coating of one or more metals or alloys,
ii) an optional second coating of a mixture of one or more ceramics and one or more metals or alloys,
iii) a third coating of one or more ceramics, and
iv) a fourth coating of one or more precious metals or alloys thereof, the fourth coating being substantially non-porous.

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This invention relates to an article for use at high temperatures and in corrosive environments and in particular t a protected article. This inv ntion als relates to a method of coating metallic substrates.

The glass industry has a particular need for mat rials which hav b th good stability at high temp ratures and good corrosion resistance f r the manufacture of apparatus that contacts molten glass. Examples of such apparatus are crucibles, stirrers, crown spinners, thermocouple sheaths, etc. The difficulties encountered with apparatus which either contacts molten glass or the atmosphere above the molten glass are the high temperatures, of the order of 1000°-1600°C, the viscosity and abrasiveness of the molten glass and the reactivity of the glass itself. Molten glass will attack, for example crucibles or containers in which it is held, and this attack is most pronounced at the glass line where the glass and air interface and the surface of the glass contacts the crucible or container wall. With time the glass attacks the wall of the apparatus, eg crucible or container and forms a hollow at the glass line as shown in Figure 1 of the accompanying drawing which depicts a portion of a wall 1 of a crucible containing molten glass 2 with air 3 above the glass. At the glass 2-air 3 interface denoted by 4 the wall of the crucible has eroded 5 due to the corrosive effect of the glass. Furthermore as a result of the reactivity of the glass small fragments of the apparatus in contact with glass may break off and contaminate the glass. This is a particular disadvantage when the glass is being used for high quality products such as television tubes which should have no visible defects. The chemical attack by the molten glass may also result in metals or compounds being leached into the glass which results in undesirable discolouration.

Apparatus for use in the glass industry is often fabricated from transition or refractory metals or alloys such as nickel alloys or metals or alloys of molybdenum, tantalum, etc. in order to provide apparatus with a reasonable time period in service. Platinum group metals or alloys have also been used as the material for such apparatus since these metals and alloys have good corrosion resistance to molten glass and good thermal stability. However, the one major disadvantage with using platinum group metals is the high cost of the material itself. To overcome the disadvantage of having apparatus fabricated solely from platinum group metals and alloys apparatus is made with a metallic substrate that is coated or clad therewith, in particular with platinum. In order to provide effective protection the coating or cladding must be of sufficient thickness to protect the substrate for a service life of eg, 3-6 months. These coatings or claddings provide some protection and enable the service life to be increased. The coating or cladding of platinum however does not prevent the major problem of diffusion of oxidants through to the substrate which results in corrosion of the substrate.

Gas turbines blades operate at high temperatures between 600°C and 1100°C and in corrosive environments. A coating of ceramic applied to the blades provides some protection. However, although the ceramic coating does protect the blades from the high temperatures the ceramic coating suffers considerable corrosion. Another disadvantage is the tendency for spalling to occur with the ceramic coating lifting from the blades and becoming detached.

An object of the present invention is to provide an article with improved corrosion resistance and heat stability which overcomes at least some of the disadvantages of the prior art, especially the problem of diffusion of oxidants through to the substrate.

Accordingly the invention provides an article for use at high temperatures and in corrosive environments comprising a metallic substrate on which is deposited successively,

i) a first coating of one or more metals or alloys,

ii) an optional second coating of a mixture of one or more ceramics and one or more metals or alloys,

iii) a third coating of one or more ceramics, and

iv) a fourth coating of one or more precious metals or alloys thereof, the fourth coating being substantially non-porous.

The invention further provides a method of making an article comprising applying, successively, to a metallic substrate a first coating of one or more metals or alloys, an optional second coating of a mixture of one or more ceramics and one or more metals or alloys, a third coating of one or more ceramics and a fourth coating of one or more precious metals or alloys thereof, and making the fourth coating substantially non-porous.

References following to a metal or metals include an alloy or alloys of the metal or metals, unless otherwise indicated.

Preferably the metallic substrate is a metal that has some corrosion resistance and/or thermal stability at high temperatures such as refractory metals, eg nickel, molybdenum, tantalum, niobium or tungsten or an alloy of any of these. Other suitable alloys are high melting point intermetallics such as nickel aluminides, cobalt aluminides, tantalum aluminides, platinum group metal intermetallics etc. The metallic substrate may have a surfac oxide layer.

Th m tal f th first coating is preferably compatible with the ceramic of th s cond coating such that onc the substrate is coated th ceramic is not degrad d by the metal reacting with th ceramic. Th metal is preferably selected from metals that have one or more of the following characteristics; i) good corrosion resistance and good thermal stability, ii) good ductility and iii) thermal coefficient of expansi n intermediate the thermal

coefficient of expansion of the m tallic substrate and the ceramic of the s cond coating. Preferably the metal is such that the coating is form d with rel ase of energy, preferably by formation of an intermetallic compound. Suitable metals ar nickel-aluminium, nickel-chr mium, palladium-aluminium, hafnium-aluminium, titanium, tantalum and palladium. Most preferred is an alloy of nickel 80wt% aluminium 20wt%.

The first coating may be deposited onto the substrate by known methods of application such as thermal spraying and in particular flame or vacuum- or air-plasma spraying.

The second coating comprises a mixture of one or more ceramics and one or more metals. Preferably the ceramic consists essentially of at least one of alumina, magnesia, hafnia, thoria and zirconia. Most preferably the ceramic consists essentially of alumina. Optionally the ceramic may include a minor amount of one or more of yttria, silica, titania and calcia. Most preferably the ceramic is of high purity of the order of 99% purity. The metal is preferably the same metal as that of the first coating. Preferably the second coating has a composition in which the proportion of metal to ceramic decreases in gradations from that at the interface adjacent the first coating to that at the interface adjacent the third coating. The second coating may be formed by thermal spraying, for example by vacuum- or air-plasma spraying and in particular the coating may be formed by the deposition of one or more layers. A plurality of layers can be employed to form a step-wise gradation of the metal to ceramic ratio as mentioned above.

The third coating of ceramic preferably consists essentially of alumina. Suitable other materials for the third coating may be magnesia, hafnia, thoria or zirconia or a mixture thereof. Optionally the ceramic may include a minor amount of one or more of yttria, silica, titania and calcia. This coating may be deposited by thermal spraying and in particular by flame or vacuum- or air-plasma spraying one or more layers.

The fourth coating is substantially non-porous and is chosen from one or more of the precious metals. Preferably the coating is of platinum. An alloy of platinum may also be used, eg platinum with 5% gold, or zirconia grain stabilised (ZGS) platinum. Other platinum group metals may also be employed. The coating may be deposited for example by flame or vacuum- or air-plasma spraying, as a powder, or by plating. Preferably the coating is applied by thermal spraying and in particular by flame or vacuum- or air-plasma spraying. The coating can be made non-porous by after treatment. The after treatment may comprise shot peening, melt glazing, hot isostatic pressing (hip) or cold isostatic pressing (cip). The thickness of the fourth coating is typically, between 75 and 200μm; however, there is no upper limit as to how thick the fourth coating may be. Preferably, the thickness of the fourth coating is at least 90μm.

Usually the article consists of the metallic substrate and the four specified coatings. However, in some cases, only the first, third and fourth coatings need be employed.

In a particular embodiment, the article has an additional fifth coating between the third and fourth coatings, the fifth coating being a mixture of one or more ceramics and one or more precious metals or alloys thereof. Preferably the ceramic consists essentially of alumina. Other suitable ceramics may be magnesia, hafnia, thoria or zirconia or a mixture thereof. Optionally the ceramic may include a minor amount of one or more of yttria, titania, silica, and calcia. Most preferably the ceramic is of high purity, of the order of 99% purity. Preferably the fifth coating has a composition in which the proportion of metal to ceramic increases in gradations from that at the interface with the third coating to that at the interface with the fourth coating. The fifth coating may be formed by thermal spraying, for example by flame or vacuum- or air-plasma spraying and in particular the coating may be formed by the deposition of one or more layers. A plurality of layers can be employed to form a step-wise gradation of the metal to ceramic ratio as mentioned above.

Figure 2 is a cross-section of an article according to the present invention.

An embodiment of the present invention is shown in Figure 2. A metallic substrate 10 has a first coating 11 of a metal or alloy, a second coating 12 of a mixture of one or more metals and alloys at least one ceramic, a third coating 13 of at least one ceramic and a fourth non-porous coating 14 of precious metal or alloy. In the second coating 12 the proportion of metal or alloy to ceramic decreases from this interface with the first coating 11 to the interface with the third coating 13 as schematically depicted with '-' for metal or alloy of the first and second coatings and '+' for the ceramic of the second and third coatings.

The invention will now be described by way of example only.

COMPARATIVE EXAMPLE A

Nicrobell A is the trade name of a $Cr/Al/Ti/Y_2O_3/Fe$ alloy, produced by Nicrob ll Pty Ltd.

Nicr bell X is the trad name of a Cr/Si/Mg/Ni alloy produced by Nicrobell Pty Ltd.

A number of test samples of refractory all ys in th form of tubes were coated with a platinum coating of various thicknesses. The platinum was deposited by means of a fused salt plating bath. One of the samples, Nicrobell A with a platinum coating of 60μm had been subject d to a preoxidation treatment so that the Nicrobell A substrate had a thin oxid layer on to which th platinum was applied. Th samples were tested by placing

the sample in contact with molten bottle glass at a temp ratur of 1200°C for a peri d of time. Each sample was placed with one end in an alumina crucible and bottle glass powder added such that n h ating th crucibl to a temp rature of 1200°C a p rtion of the sample is in contact with molten glass. At th nd of the test th samples were visually examined t se the corrosive effect on the sample by the glass. Th results for a 24 hour test are given in Table 1 below. The alloys Nicrobell X and Nicrobell A consist of chromium 20%, aluminium 4.5%, titanium 0.5%, Y_2O_3 0.5%, remainder iron, and chromium 14.0%, silicon 1.4%, magnesium 0.2% and remainder nickel, the percentages being by weight.

Table 1

Substrate	Pt Coating Thickness µm	
Nicrobell A	46	Ni diffused through Pt coating.
Nicrobell A	60	Pt coating lifted off by diffusion.
Nicrobell X	72	Fe diffused through Pt coating.
		Al reaction with Pt.

The results of the tests given in Table 1 above show that a single coating of platinum between 46µm and 72µm onto a metallic substrate does not prevent corrosion by molten glass.

<u>Examples 1-12</u>

A number of tubes were fabricated from a commercial nickel-based alloy, nickel 75wt%, chromium 25wt%. A first coating of nickel was applied thereto followed by a second coating of nickel and alumina formed by three layers having the $Ni:Al_2O_3$ proportions 1:1, 1:3 and 1:9 respectively. The third coating of alumina was applied as one or more layers. The first, second and third coatings were applied using vacuum plasma spraying. Examples 1 to 4 were provided with a conductive surface by sputter deposition of 0.2µm films of platinum in preparation for a fourth coating of platinum deposited by electro-deposition from a bath of composition disclosed in Example of EP 0358375 A with 5-5.5g of platinum per litre. Examples 1, 2 and 3 had an additional top coating of 0.2µm of gold deposited by sputtering. The fourth coating of Examples 5 to 8 was applied by a fused salt process. Examples 9-12 had the fourth coating deposited by flame spraying. The Examples were tested for 300 hours by contacting with molten glass as described in Comparative Example A and the results are given in Tables 2, 3 and 4. AGL, GL and BGL denote 'Above Glass Line', 'Glass Line' and 'Below Glass Line'.

TABLE 2

DURATION OF TEST - 300 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	+Au 0.2µm	Coating Condition After Test	
1	Ni75%/Cr25%	1	1	1	2	18.0	Yes	AGL	Coating peeled back, substrate still intact, Pt coloured.
								GL	Coating eroded, substrate not corroded.
								BGL	Coating generally detached. Glass colour - green.
2	Ni75%/Cr25%	1	1	1	1	18.1	Yes	AGL	Coating blistered, blackened, still intact.
								GL	Some erosion through coating. Substrate protected.
								BGL	Still intact, loosened on cooling. Glass colour - green.
3	Ni75%/Cr25%	1	1	1	4	17.5	Yes	AGL	Darkened (Ni/Cr diffusion through Pt) intact but lifted.
								GL	Attacked but layer intact - substrate protected.
								BGL	Intact but some cracking. Glass colour - green.

TABLE 2 continued

DURATION OF TEST - 300 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	2nd Coating $Ni:Al_2O_3$ 1:3	2nd Coating $Ni:Al_2O_3$ 1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	+Au 0.2µm	Coating Condition After Test	
4	Ni75%/Cr25%	1	1	1	2	11.0	No	AGL	Darkened (Ni/Cr diffusion through Pt), intact but lifted.
								GL	Substrate protected - coating blistered severely.
								BGL	Pt protected sample. Intact. Glass colour - green.

TABLE 3

DURATION OF TEST - 200 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	2nd Coating $Ni:Al_2O_3$ 1:3	2nd Coating $Ni:Al_2O_3$ 1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness	After treatment		Coating Condition After Testing
5	Ni75%/Cr25%	1	1	1	2	51	-	AGL	Generally intact but black crystalline surface.
								GL	Slight blistering.
								BGL	General protection. Glass colour - green.
6	Ni75%/Cr25%	1	1	1	1	54	-	AGL	Generally very good and intact, but black crystalline.
								GL	Slight blistering/breakdown.
								BGL	Some Ni diffusion but very protective, very adherent. Glass colour - green/brown.
7	Ni75%/Cr25%	1	1	1	4	59	Shot peened	AGL	Blistered mostly bright Pt coloured.
								GL	Intact, slight blistering.
								BGL	Slight spallation - general protection. Glass colour - green/brown.

TABLE 3 continued

DURATION OF TEST - 200 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness	After treatment	Coating	Condition After Testing
8	Nimonic	1	1	1	2	63	-	AGL	Blistered but excellent bright - colour.
								GL	Blistered but bright.
								BGL	Blistered, bright. Glass colour - clear green/brown.

TABLE 4

DURATION OF TEST - 402 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	Coating Condition After Testing
9	Ni75%/Cr25%	1	1	1	2	112	AGL Mainly as before test. GL Slight erosion, but OK. BGL Glass adheres but could be ocked off. Coating generally intact. Glass colour - pale green.
10	Ni75%/Cr25%	1	1	1	1	88	AGL Significant colouration. GL Slight erosion. BGL Glass adheres. Glass colour - mid/dark green.
11	Ni75%/Cr25%	1	1	1	4	115	AGL Significant colouration. GL Visible but not significantly different from BGL. BGL Glass adheres but can be removed. Glass colour - dark green/brown.

TABLE 4 continued

DURATION OF TEST - 402 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	Coating Condition After Testing	
12	Ni75%/Cr25%	1	1	1	2	120	AGL	Blackened colouration and blistering.
							GL	Slight blistering but generally as BGL.
							BGL	Glass adheres, coating fragments on trying to remove glass. Glass colour - dark green/brown.

C nclusi n

Exampl s 1-12 demonstrat that the four-lay r coating system is capable f prot cting base metal substrate. H wever, very thin fourth coatings w re largely in ffective b low th glass line.

Comparative Examples B and C

Example 13

Example 13 comprised a closed end tube of Nicrobell A with a first coating of Ni 96wt% Al 4wt%, a second coating of nickel and alumina formed by three layers having Ni:Al_2O_3 proportions of 1:1, 1:3 and 1:9, a third coating of alumina and a fourth coating of platinum of thickness 6.1μm. Comparative Example B was a tube of Nicrobell A with a first coating of Ni 96wt% Al 4wt%, a second coating of alumina graduated from low to high density and a third coating of platinum of thickness 4.8μm. For Comparative Example C a Nicrobell A closed end tube was coated with a first coating of alumina graduated from low to high density and a second coating of platinum, thickness 5.5μm. The coatings of Ni 96wt% Al 4wt%, alumina and nickel and alumina were applied by vacuum plasma spraying. After the surface was rendered conductive by sputter-deposition of a sub-micron film of platinum, the fourth coatings of platinum were deposited by electro-deposition from a bath of composition as described in Example 1 of EP 0358375 A with 5-5.5g of platinum per litre. These examples were tested for 300 hours by contacting the tubes with molten glass as described above in Comparative Example A and the results are given in Table 5 below. The Nicrobell A alloy has the composition chromium 14wt%, silicon 1.4wt%, magnesium 0.25wt% and remainder nickel.

TABLE 5

DURATION OF TEST - 300 Hours

Example	Substrate	1st Coating	2nd Coating	3rd Coating	4th Coating	Coating Condition After Testing
B	Nicrobell A	Ni96% Al4%	Al_2O_3 graduated low to high density	Pt 4.8μm	-	AGL Coating flaked off on cooling. GL Substantial glass line erosion of ceramic coating. BGL 20% of surface covered by an adherent alumina layer.
C	Nicrobell A	Al_2O_3 graduated low to high density	Pt 5.5μm	-	-	AGL Coating flaked off on cooling. GL Substantial glass line erosion of ceramic coating.
13	Nicrobell A	Ni 96% Al 4%	3 layers of Ni & Al_2O_3 proportions 1:1 1:3 1:9	Al_2O_3	Pt 6.1μm	AGL Coating flaked off on cooling. GL Substantial glass line erosion of ceramic coating. BGL 90% of surface covered by an adherent alumina layer.

The r sults given in Table 5 above indicate that to provide articles which can be used at high temperatures and in corrosiv nvironments four diff rent specific coatings ar r quired. Whil in each case th Pt lay r was too thin to be ff ctiv , and flak d off, th third layer was significantly m re intact in the four coating Exampl as compared with the thr coating Comparative Exampl .

Examples 14-21

Examples 14 to 21 employed closed end tubes of Nicrobell A or Nicrobell C as substrates. Nicrobell C is the trade name of an alloy of composition chromium 23.9wt%, silicon 1.75wt%, magnesium 0.15wt%, niobium 0.49wt% and remainder nickel, produced by Nicrobell Pty Ltd. The composition of the first coating for these examples was nickel 80wt%, aluminium 20wt%. The second coating of Ni 80wt% Al 20wt% and alumina was deposited as three layers with various proportions of Ni 80wt%, Al 20wt%: alumina. Details are given in Table 6 below. Between 4 and 30 layers of alumina were deposited to form the third coating. The first, second and third coatings were deposited by vacuum plasma spraying. The fourth layer of platinum was formed by flame-spraying followed by an after treatment of shot-peening to ensure the fourth coating was substantially non-porous.

The examples were tested by contacting them with molten glass for 300 hours as described above. The results are given in Table 6 below.

TABLE 6

DURATION OF TEST - 300 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers µm	4th Coating Pt thickness	Coating Condition After Testing
14	Nicrobell A	1	1	1	4	111	AGL Good. GL Glass adheres - no other attack. BGL Slight diffusion generally OK. Glass colour - pale green.
15	Nicrobell A	1	1	1	12	98	AGL Good. GL Glass adheres - no other attack. BGL Patchy diffusion generally OK. Glass colour - pale green.
16	Nicrobell A	1	1	1	30	120	Not Tested.

TABLE 6 continued

DURATION OF TEST - 300 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	2nd Coating $Ni:Al_2O_3$ 1:3	2nd Coating $Ni:Al_2O_3$ 1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	Coating Condition After Testing	
17	Nicrobell A	-	3	-	12	123	AGL	Very slight exfoliation, generally good.
							GL	Glass aderes, but otherwise OK.
							BGL	Slight diffusion (Patchy) generally very good.
18	Nicrobell A	-	-	3	4	91	AGL	Good.
							GL	Glass adheres, otherwise OK.
							BGL	Some diffusion.
19	Nicrobell A	-	-	3	12	117	AGL	Some exfoliation, but generally good.
							GL	Glass adheres, but otherwise OK.
							BGL	Slight diffusion (Patchy) but generally very good. Glass colour - pale green.

TABLE 6 continued

DURATION OF TEST - 300 Hours

Example	Substrate	2nd Coating $Ni:Al_2O_3$ 1:1	1:3	1:9	3rd Coating No of Al_2O_3 Layers	4th Coating Pt thickness µm	Coating Condition After Testing	
20	Nicrobell C	1	1	1	4	102	AGL	Completely intact, no noticeable change.
							GL	Boundary line visible, but looks OK.
							BGL	Few areas of diffusion (green) but generally very good.
								Glass colour - pale green.
21	Nicrobell C	-	-	3	12	104	AGL	Slight diffusion but OK except where cracked open during cooling.
							GL	No significant attack.
							BGL	Glass adheres - some areas of diffusion, especially bottom.
								Glass colour - pale green.

Exampl 16 was not test d as cracks appeared prior to platinum coating. This was probably due to th thickness of th third coating which was form d from thirty layers of alumina. Th results btained for Exampl s 14, 15 and 20 with a second coating having the amount of metal decreasing from the interface with th first coating to th interface with th third coating are b tter than f r Exampl s 17, 18, 19 and 21 where the prop rtion of metal to ceramic was the same through the thickness of the second coating.

Example 22-25

Examples 22-25 employed substrates of Nicrobell C. The first coat for each was nickle 80wt%, aluminium 20wt%. Examples 22-24 employed second coats of Ni 80wt% Al 20wt% and alumina deposited in the ratios 1:1, 1:3 and 1:9, and third coats, of 8 layers of either alumina or zirconia. Example 25 omitted coats 2 and 3. The first, second, and third coats were deposited by vacuum plasma spraying. The fourth layer of Pt or Pt/5wt% Au was flame sprayed followed by shot peening to ensure that the fourth layer be substantially non-porous.

The examples were tested in molten glass at 1200°C for 400 hours, the results are given below.

DURATION OF TEST -400 Hours

Coatings

ID	Substrate	1st coat	2nd 1st:3rd 1:1, 1:3, 1:9	3rd No. of Al_2O_3	4th PGM	thickness
22	Nicrobell C	Ni20%Al	1/1/1	8	Pt	81μm
23	Nicrobell C	Ni20%Al	1/1/1	8	Pt	176μm
24	Nicrobell C	Ni20%Al	1/1/1	8	Pt/Au	76μm
25	Nicrobell C	Ni20%Al	-	-	Pt	99μm

Results- Coating condition after test

22. AGL good, intact. Pt too thin to withstand cooling
    GL no different to BGL
    BGL glass adheres- on cooling in situ Pt partially cracks
    Glass colour - green, substrate protected.

23. AGL very good, completely intact
    GL glass adheres
    BGL glass adheres- on cooling however coating stays intact
    Glass colour - pale green, substrate protected.

24. AGL cracked, due to lack of ductility on cooling
    GL coating comes off on cooling
    BGL minimal adherence of glass, cracks on cooling
    Glass colour - green, substrate protected.

25. AGL mauve, brown due to Ni/Cr diffusion through Pt

GL Pt in colour, glass coloured

BGL coating OK

Glass colour - dark green, substrate not proected.

The results obtained for Examples 22, 23 and 24 show that the coatings have protected the substrates from molten glass attack, the thicker the platinum group metals (PGM) layer (Example 23) the better the degree of protection. A thicker layer of PGM gives more ductility. Adequate PGM coating ductility is essential to promote protection.

Example 26-28

Examples 26-28 are components to be used in temperature measurement. They were manufactured using Nicrobell C substrates, for trials in an industrial glass bottle manufacturing plant. The coating system applied was identical to that for Example 23. The example components were placed in a forehearth containing flowing molten flint glass at a temperature which ranged from 1130-1160°C for varying times. The details are given below.

ID	Substrate	1st coat	2nd 1st:3rd 1:1, 1:3, 1:9	3rd No. of layers Al_2O_3	4th PGM thickness	Duration of test	Typical temperature °C
26	Nicrobell C	Ni20%Al	1/1/1	8	Pt 169μm	24 hrs	1137°C
27	Nicrobell C	Ni20%Al	1/1/1	8	Pt 171μm	100 hrs	1160°C
28	Nicrobell C	Ni20%Al	1/1/1	8	Pt 174μm	1000 hrs	1160°C

Results- Coating condition after test

After testing all Examples (26-28) were completely intact, no corrosion had occurred nor cracking on cooling. The example components had been removed from the molten glass before cooling unlike the laboratory tests where the examples cooled in situ. The glass below the glass line had not adhered to the samples evenly. Some areas had been left completely free of glass. On cooling, particularly Example 28, the attatched glass cracked and fell away from the metal surface. The coating was concluded to have 'nonstick' characteristics. This is an added advantage reducing any cross-contamination and aiding recycling and examination of the components.

Example 29-32

Examples 29-32 employed substrates of Nicrobell C. The first coat was nickle 80wt%, aluminium 20wt%, the second coats were Ni 80wt%, Al 20wt% and alumina deposited in the ratios 1:1, 1:3 and 1:9. The third coats were 8 layers of alumina. The first, second, and third coats were deposited by vacuum plasma spraying. The fourth layers, of Pt or Pt/5wt% Au were flame sprayed, with this coating in some cases being completed by deposition f ZGS Pt r PT 5wt%Au. This was foll w d by shot pe ning to ensure that th outer m tal coating be substantially non-por us.

The examples w re tested in molten glass in th laboratory at 1200°C f r 400 hours, the results are giv n bel w.

DURATION OF TEST -400 Hours

I.D	Substrate	1st coat	Coatings 2nd 1st:3rd 1:1, 1:3, 1:9	3rd No. of layers Al_2O_3	4th PGM thickness
29	Nicrobell C	Ni20%Al	1/1/1	8	Pt 85µm + ZGS Pt 69µm
30	Nicrobell C	Ni20%Al	1/1/1	8	Pt 82µm + Pt/5%Au 100µm
31	Nicrobell C	Ni20%Al	1/1/1	8	Pt/5%Au 121µm
32	Nicrobell C	Ni20%Al	1/1/1	8	Pt/5%Au 158µm

Results- Coating condition after test

29. AGL good, intact coating

GL no corrosion

BGL slight deformation in coating due to cooling in situ, no diffusion

Glass colour - pale green, substrate protected.

30. AGL good, intact coating

GL no corrosion

BGL good intact coating, however a slight grey surface appearance

Glass colour - pale green, substrate protected.

31. AGL single cooling crack

GL no obvious effect

BGL a grey surface appearance.

Glass colour - green, substantially protected.

32. AGL good coating

GL no obvious change

BGL a white grey surface appearance but intact

Glass colour - pale green, substrate protected.

The results for Examples 30-34 indicate that a molten glass resistant coating can produced from ZGS Pt. To achieve protection with Pt 5wt%Au a considerably thicker metal coating is required than with Pt alone.

Example 33-38

The substrate employed in Examples 33-38 were selected from Nicrobell C and MA956 alloy closed end tubes. MA956 is the trade name of an alloy of composition Fe 74wt%, Cr 20wt%, Al 4.5wt%, Ti 0.5wt% and Y_2O_3 0.5wt% produced by Inco Alloys Ltd. The first coat was nickel 80wt%, aluminium 20wt% or nickel 95.5wt%, aluminium 4.5wt%, deposited by vacuum plasma spraying (VPS) and air plasma spraying (APS) respectively. For the APS samples in this instance the second coating was absent however for Example 37 the coating system was as in examples 27-29. The third layer was of alumina of thicknesses 120-245 µm. The fourth layer of Pt was deposited and processed as per Examples 27-29. The examples were tested in molten glass for 200 hrs at 1200°C, details presented below.

DURATION OF TEST -200 Hours

			Coatings			
ID	Substrate	Spraying Technique	1st coat	2nd $Ni:Al_2O_3$ 1:1, 1:3, 1:9	3rd No. of Al_2O_3	4th PGM thickness
33	Nicrobell C	APS	Ni4.5%Al	-	135µm	Pt 148µm
34	Nicrobell C	APS	Ni4.5%Al	-	245µm	Pt 159µm
35	MA956	VPS	Ni20%Al	1/1/1	160µm	Pt 138µm
36	MA956	VPS	Ni20%Al	-	160µm	Pt 160µm
37	MA956	APS	Ni4.5%Al	-	220µm	Pt 164µm
38	MA956	APS	Ni4.5%Al	-	120µm	Pt 166µm

The thickness of the ceramic layers that have been quoted in all the previous examples are in layers. An approximate converation factor is that one layer is equal to 20µm.

Results - Coating condition after test

33. AGL Ni/Cr diffusion present- no cracks

GL Diffusion but coating intact

BGL coating OK

Glass colour - green, substrate substantially protected.

34. AGL Very slight Ni/Cr diffusion

GL good coating

BGL good coating

Glass colour - pale green, substrate protected.

35. AGL no observable effect

GL no observable effect

BGL no observable effect

Glass colour - pale green, substrate protected.

36. AGL no observable effect

GL no observable effect

BGL no observable effect

Glass colour - pale green, substrate protected.

37. AGL localized failure with breakaway oxidation

GL coating OK, no diffusion

BGL coating OK, no diffusion

Glass colour - pale green, substrate essentially protected.

38. AGL coating disrupted in localised zones

GL coating ok

BGL coating ok

Glass colour - pale green, substrate essentially protected.

For the short duration no noticeable difference occured between the VPS examples without or with the barrier layer. The APS examples indicate that as long as sufficient thickness of barrier layer is laid down, to offset of increased porosity, protection is given. Examples 35-36 indicate, iron based alloys, such as the corrosion resistant alloy MA956, can be given additonal protection for service in molten glass enviroment by application of a coating system according to this invention.

Claims

1. An article for use in high temperature corrosive environments comprising a metallic substrate on which is deposited successively,
   i) a first coating of on r more metals or alloys,
   ii) an pti nal second coating of a mixture of on or more ceramics and one or mor metals or alloys,
   iii) a third coating of one or more c ramics, and
   iv) a fourth coating of ne or more precious metals or alloys thereof, the fourth c ating being substantially non-porous.

2. An article according t claim 1 wherein the metallic substrate has deposit d all four said coatings.

3. An article according to claim 1 r 2 wher in the first coating is of a metal r alloy select d from nickel-aluminium, nickel-chromium, palladium-aluminium, hafnium-aluminium, titanium, tantalum and palladium.

4. An article according to claim 3 wherein the first coating is of an alloy of nickel 80wt% aluminium 20wt%.

5. An article according to any preceding claim wherein the ceramic of the second and third coatings is alumina.

6. An article according to claim 5 wherein the ceramic is of purity 99%.

7. An article according to any proceding claim wherein the second coating has a composition in which the proportion of metal to ceramic decreases from the interface adjacent the first coating to the interface adjacent the second coating.

8. An article according to any preceding claim wherein the fourth coating is of platinum or an alloy of platinum.

9. An article according to any preceding claim wherein the fourth coating is of platinum.

10. An article according to any preceding claim in contact with molten glass or the atmosphere above molten glass.

11. A method of making an article claimed in any of the preceding claims comprising applying, successively, to a metallic substrate a first coating of one or more metals or alloys, a second coating of a mixture of one or more ceramics and one or more metals or alloys, a third coating of one or more ceramics and a fourth coating of one or more precious metals or alloys thereof, and making the fourth coating substantially non-porous.

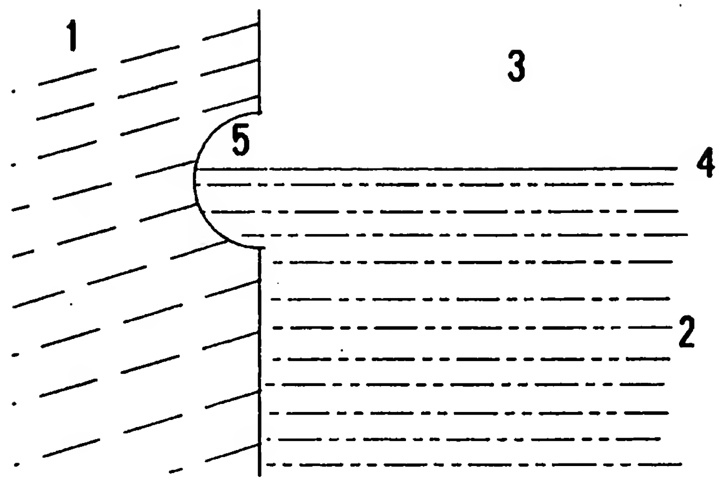

FIGURE 1

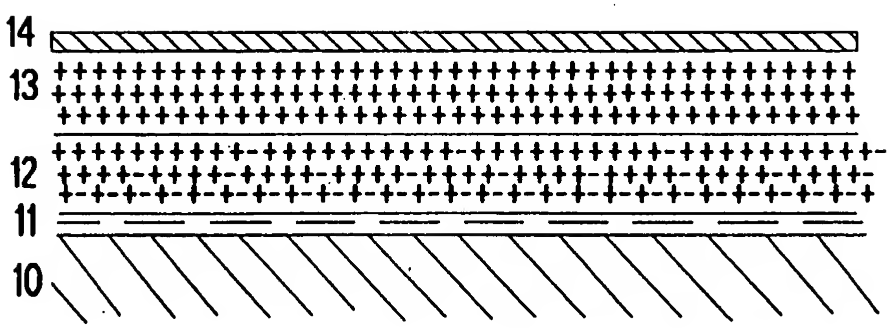

FIGURE 2